

AMINO ACIDS IN THE ANTARCTIC MARTIAN METEORITE MIL03346. D. P. Glavin¹, A. Aubrey², J. P. Dworkin¹, O. Botta³, J. L. Bada², ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, daniel.p.glavin@nasa.gov, ²Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, ³International Space Science Institute, Hallerstrasse 6, CH-3012 Bern, Switzerland.

Introduction: The report by McKay et al. [1] that the Martian meteorite ALH84001 contains evidence for life on Mars remains controversial. Of central importance is whether ALH84001 and other Antarctic Martian meteorites contain endogenous organic compounds. In any investigation of organic compounds possibly derived from Mars it is important to focus on compounds that play an essential role in biochemistry as we know it and that have properties such as chirality which can be used to distinguish between biotic versus abiotic origins. Amino acids are one of the few compounds that fulfill these requirements.

Previous analyses of the Antarctic Martian meteorites ALH84001 and EETA79001 have shown that these meteorites contain low levels of terrestrial amino acid contamination derived from Antarctic ice meltwater [2,3]. Here we report preliminary amino acid investigations of a third Antarctic Martian meteorite MIL03346 which was discovered in Antarctica during the 2003-04 ANSMET season.

Samples and Analytical Techniques: The Antarctic Nakhla MIL03346 was provided by the meteorite curator at the NASA Johnson Space Center. A single fragment of MIL03346 (split 38, parent 0) weighing 1.0 g was crushed into a fine powder with an annealed (500°C overnight) mortar and pestle in a positive pressure (1- μ m filtered air) clean room and then transferred to a clean vial. Crushed serpentine (a hydrated magnesium silicate) that had been heated at 500°C for several hours was used as a procedural blank. For reference samples, a sample of the Antarctic Martian meteorite ALH84001, the Martian meteorite Nakhla, the Antarctic CM carbonaceous chondrite LEW90500, and a surface ice sample collected during the ANSMET 2003-04 season at La Paz ice field, Antarctica were processed in parallel with MIL03346.

Amino acids and their enantiomeric abundances were investigated in MIL03346, in the meteorite control samples, and in blanks using high performance liquid chromatography (HPLC) coupled with UV-fluorescence detection at the Scripps Institution of Oceanography (SIO) and using liquid chromatography-time of flight-mass spectrometry (LC-ToF-MS) at the NASA Goddard Space Flight Center (GSFC). A portion of each sample (~200 mg) was sealed in a clean glass test tube with 1 ml of

double-distilled water for 24 h in a heating block set at 100°C. The ampoules were cracked open and centrifuged to separate out the particulate from the water supernatant. One half of the water extract was transferred to a new test tube, dried under vacuum and desalted by using cation exchange resin (AG50W-X8, 100-200 mesh, Bio-Rad) prior to HPLC analysis to determine the abundance of free amino acids associated with the bulk sample (unhydrolyzed water soluble fraction). The remaining water supernatant was transferred to a separate test tube, dried under vacuum, hydrolyzed under 6 M HCl vapor at 150°C for 3 h, desalted, and analyzed by using OPA/NAC derivatization and HPLC separation to determine bound amino acids in the bulk sample (hydrolyzed water-soluble fraction) [4].

Results and Discussion: The HPLC analyses of MIL03346 revealed that trace levels of L-aspartic and glutamic acids, glycine, and L-alanine were present in the 6M HCl hydrolyzed hot water extract at a concentration of ~150 ppb (Fig. 1). A similar distribution and concentration of amino acids was detected in ALH84001, consistent with a previous analysis of this meteorite [2]. Several amino acids were identified in Nakhla that were not detected in ALH84001 and MIL03346, including D-aspartic acid, D-glutamic acid, D-alanine, β -alanine, and γ -amino-*n*-butyric acid. However, the presence of these amino acids in the Nile Delta sediment collected near the fall locality of Nakhla, strongly suggests that the amino acids in Nakhla are terrestrial in origin [4].

In contrast to the Martian meteorites, a much more diverse set of amino acids was found in the Antarctic carbonaceous chondrite LEW90500, which is consistent with the results of previous investigations of this meteorite [5]. The amino acid α -aminoisobutyric acid (AIB) which is present at a concentration of ~2,800 ppb in LEW90500, and is characteristic of an amino acid of apparently extraterrestrial origin, were not identified in any of the extracts of MIL03346, ALH84001, or Nakhla. However, one peak that was not detected in any of the procedural blanks, was observed in the acid hydrolyzed hot water extracts of LEW90500, ALH84001, Nakhla, and MIL03346 (marked 'X' in Fig. 1). This unidentified compound could be an amine, since only compounds containing a primary amine group are detected by the OPA/NAC

derivatization and HPLC separation method. This peak was not observed in any of the unhydrolyzed water extracts, which either indicates that this compound is only present in bound form or was synthesized during the acid hydrolysis procedure. A similar peak had also been found in a previous examination of ALH84001, however the mass of the compound was not determined. We are presently analyzing these meteorite extracts at GSFC using an LC-ToF-MS instrument to determine the exact mass of this compound. We are also in the process of analyzing the Antarctic ice sample to determine whether or not this amine compound is present.

Conclusions: We have identified very low levels of amino acids in the Antarctic Nakhla MIL03346. Most of these amino acids are likely terrestrial in origin, derived from ice meltwater percolating through the meteorite during its residence time in Antarctica. We have not yet been able to identify an amine compound that is present in the hydrolyzed extract of MIL03346 as well as the other Antarctic meteorite samples. Future analyses of ice recently collected from La Paz, Antarctica may help determine whether or not this compound is indigenous to these Antarctic meteorites. Furthermore, we hope to be able to identify this compound by its exact mass using LC-ToF-MS. These results will be presented.

References: [1] McKay D. S. et al. (1996) *Science*, 273, 924-930. [2] Bada J. L. et al. (1998) *Science*, 279, 362-365. [3] McDonald G. D. and Bada J. L. (1995) *Geochim. Cosmochim. Acta*, 59, 1179-1184. [4] Glavin D. P. et al. (1999) *Proc. Natl. Acad. Sci. USA*, 96, 8835-8838. [5] Botta O. and Bada J. L. (2002) In *Lunar and Planetary Science XXXIII*, abstract #1391, LPI, Houston (CD-ROM).

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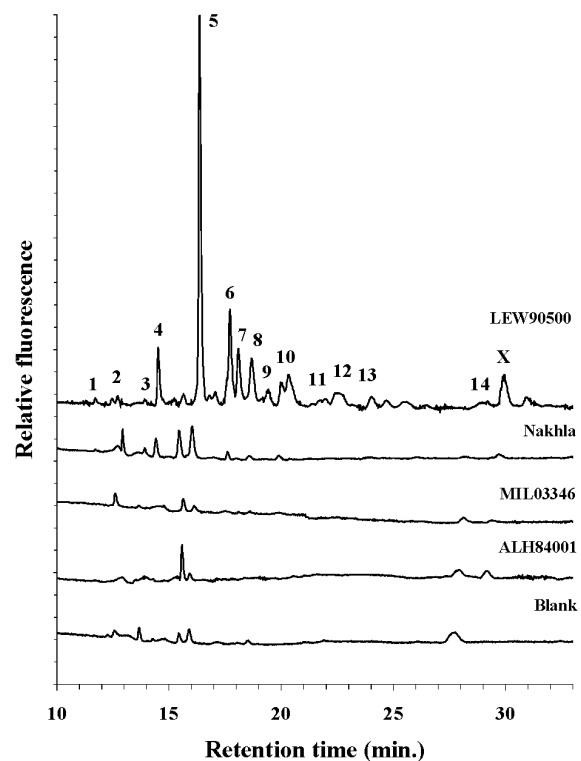


Figure 1. The 10- to 33-min region (no peaks were observed outside of this time period) of the HPLC chromatograms from the SIO analysis. OPA/NAC derivatization (1 min.) of amino acids in the 6M HCl-hydrolyzed hot water extracts from the Antarctic CM carbonaceous chondrite LEW90500, the Martian meteorite Nakhla, the Antarctic Martian meteorites MIL03346 and ALH84001, and the serpentine blank. The peaks were identified by comparison of the retention times to those of an amino acid standard run in parallel, as follows: 1, D-aspartic acid; 2, L-aspartic acid; 3, DL-serine; 4, DL-glutamic acid; 5, glycine; 6, β -alanine; 7, D-alanine; 8, L-alanine; 9, γ -amino-*n*-butyric acid; 10, DL- β -amino-*n*-butyric acid; 11, α -aminoisobutyric acid (AIB); 12, DL- α -amino-*n*-butyric acid; 13, DL-isovaline; 14, methylamine; and X, unknown primary amine.